DEVICES AND PROCESS FOR HIGH-PRESSURE MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority from U.S. Provisional Application No. 61/422,599 entitled "System and Process for High Pressure Magic Angle Spinning Nuclear Magnetic Resonance", filed 13 Dec., 2010, incorporated in its entirety herein.

STATEMENT REGARDING RIGHTS TO INVENTION MADE UNDER FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

This invention was made with Government support under Contract DE-AC05-76RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates generally to magic angle spinning (MAS) spectroscopy and magnetic resonance imaging. More particularly, the present invention relates to a high-pressure magic angle spinning rotor and process for high-pressure magic angle spinning nuclear magnetic resonance spectroscopy and imaging.

BACKGROUND OF THE INVENTION

Nuclear Magnetic Resonance (NMR) spectroscopy and imaging are powerful tools for obtaining detailed molecular structure and dynamics information for samples under investigation. NMR methods address numerous chemical, physical, and biological problems across various scientific disciplines. Magic Angle Spinning (MAS) is one of the most widespread NMR methods and is the only technique that allows a high resolution NMR spectrum to be acquired on solids, semi-solids, and mixtures of various sample materials. In MAS NMR, a sample is spun at a sample spinning rate of several kHz or more about an axis inclined at an angle of 54.74 degrees (°) with respect to the main magnetic field. Sample spinning speeds are used to average out line-broadening effects arising from common shielding interactions including, e.g., chemical shift anisotropic-gradients, dipolar-gradients, and magnetic-susceptibility gradients to give high-resolution NMR spectra. However, despite its wide spread application, MAS has not yet been reported in the literature at high-pressure conditions exceeding 70 bar due to various technical challenges that remain to be addressed. First, sample carriers cannot be made of metals due to strong eddy currents associated with a spinning metal in a strong magnetic field. This leaves non-metals for sample carriers including glasses, ceramics, and polymer plastics. Early development efforts in high-pressure MAS NMR investigated segmental motion of polymers (i.e., interchain distances within polymers) that were plasticized by dense gases. The sample carrier was a glass tube insert in which gas was cryogenically transferred into the carrier using a standard volumetric absorption method. The carrier was then flame-sealed or epoxy-sealed and subsequently inserted into a MAS rotor and balanced with KBr powder. The carrier was pressurized with xenon (Xe) and CO_2 gases. However, (i) reactions under a constant pressure were not obtained, (ii) maximum upper pressure was limited due to the use of thin glass tubes, and (iii) the carrier could not be re-opened to recharge and continue the sample reactions. A later carrier insert was made of DELRIN™ polymer that included an internal seal. The DELRIN™ insert included a cylindrical design that was inserted into a ceramic MAS rotor after pressurization. A 94.2 MHz ^{19}F MAS spectrum of CH_3F gas was acquired using this carrier insert. However, significant penetration by the CH_3F molecules into the DELRIN™ polymer material was observed over time, with a corresponding reduction in pressure. Similar penetration problems have been reported in the literature with CO_2 and N_2O gases using MAS inserts made from the polymer PEEK®. In these experiments, pressure was limited because a fast sample spinning of several kHz or more was required. The sample rotor required a small diameter, which complicated the sealing necessary to attain high-pressures with this design. Polymer inserts made of polymers such as DELRIN™ and PEEK® are commonly plagued by strong unwanted carbon and/or proton background signals which can mask desired NMR signals in systems containing carbon, protons, or both. Thus, a high-pressure rotor is needed that provides sealing at high reaction temperatures and pressures, minimizes penetrations by sample molecules and fluids at high reaction temperatures and pressures, and minimizes background signals that complicate the desired signal, permitting high-resolution NMR spectra and images to be generated. The present invention meets these needs by addressing various problems known in the art. Additional advantages and novel features of the present invention will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. Accordingly, the following descriptions of the present invention should be seen as illustrative of the invention and not as limiting in any way.

SUMMARY OF THE INVENTION

The present invention includes a high-pressure (HP) Magic Angle Spinning (MAS) rotor (HP-MAS-R) for generating high-resolution NMR spectra and images. The HP-MAS rotor of the invention includes a high-pressure rotor sleeve. The rotor sleeve is reusable, overcoming technical problems associated with prior art designs. In various embodiments, the sample rotor sleeve (cylinder) is composed of a ceramic. In some embodiments, the rotor sleeve is composed of a zirconia ceramic. In some embodiments, the rotor sleeve is composed of a silicon nitride (SiN) ceramic. The high-pressure rotor sleeve defines an integrated high-pressure sample cell. The sample cell spans the entire inner diameter of the rotor sleeve.

In some embodiments, the high-pressure rotor sleeve has an outer diameter dimension that ranges from about 4 mm to about 25 mm.

In some embodiments, the high-pressure rotor is a 9.5-mm MAS rotor that includes a high-pressure sample cell with a cell volume of at least about 350 uL.

In various embodiments, the sample cell includes various lengths providing variable sample volumes. The sample cell maintains a selected high pressure with the rotor when sealed.

In various embodiments, the rotor sleeve includes at least one grooved surface along the inner wall of the rotor sleeve positioned adjacent the sample, cell. In some embodiments, a grooved surface is positioned above and below the sample cell along the length of the inner wall of the rotor sleeve. In some embodiments, the grooves are micro-grooves. In a preferred embodiment, at least one threaded sealing member is secured adjacent grooves along the inner wall of the rotor sleeve with a high-pressure adhesive. The adhesive is prefer-